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AGING CHARACTERISTICS OF Li/SO_2 CELLS

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Introduction

Delays in the launch of the Galileo probe to Jupiter have resulted in a new trajectory that will increase the fly-out time such that batteries will be greater than seven years old at the time of descent into the Jovian atmosphere. The longest real time data for flight design cells was five years at the time of launch.

A program was initiated to establish a methodology and data base so that the performance of these cells may be predicted at the time they are expected to complete the mission. Cells from five lots and five storage temperatures, ranging from one year to seven years in age, were studied. Chemical analysis was performed on one cell from each lot/storage group. The remaining cells in each group were discharged at the mission load and temperature. Additional cells were placed on high temperature accelerated storage, and then discharged.

In addition, cell storage data generated independently at Sandia National Laboratories was combined with the Galileo cell data. All data were statistically analyzed and an Arrhenius plot constructed.

Program Outline

Galileo cells from the following lots/storage conditions were obtained from NASA/Ames Research center and studied in this program.

Lot No.	Date of Manufacture	Storage Conditions, °C
3	1/81	0
		20
4	7/83	0
		10
		20
		30
		40
5	9/84	0
6	3/85	0
		20
7	4/87	0

Five cells from each lot/storage condition were discharged. Another cell from each group, except Lot 4, 10° and 30°C, had a premortem chemical analysis performed on it. In addition, 15 cells each from Lots 5, 6 and 7 (0°C storage) went through an accelerated aging matrix at 40°, 50° and 60°C.

Cells studied independently at Sandia were from two manufacturers and stored for up to 5 years at -40° to 0°C.

Premortem Chemical Analysis

First, each cell was x-rayed from several angles. The cell was then punctured in a special fixture and its internal pressure measured. A small gas sample was taken for mass spectroscopic analysis, and the remainder cold-trapped for SO_2 determination by iodine-thiosulfate back titration. The cell was then opened in an inert atmosphere and the electrode assembly removed. The lithium surface was examined by scanning electron microscopy and several surface analytical techniques.

The electrolyte was studied using C^{13}, O^{17} and H^1 nuclear magnetic resonance (NMR) analysis.

The cathode surface area was determined for each cell using the BET technique (nitrogen absorption). Each cathode was then studied by x-ray diffraction to determine solid products deposited in the porous carbon.

Discharge Tests

All cells in the matrix, except those undergoing premortem chemical analysis, were discharged at 4 A and 0°C to a 1.5 V cut-off. Voltage versus time plots were generated for each cell. The amp-hour capacities were calculated to 2.0 V.

The Sandia cells were discharged through a 6.25 ohm load at 25°C to a 1.5 V cut-off. The amp-hour capacities were calculated to 2.0 V.

Results and Discussion

Premortem chemical analysis. Prior to the gas analysis, the internal pressure of each cell was measured. In general, the pressure increased with the age of the cells. There was little difference in pressure between cells stored at 0° and 20°C. The one cell stored at 40°C (Lot 4) had an internal pressure ~3 psi higher than cells from the same lot stored at 0° and 20°C. The internal pressures ranged from 31-37 psi.

The gasses analyzed by mass spectroscopy were H_2, CH_4, CO, C_2H_6, CH_3CN and CO_2. The most notable trend was found with the H_2, its content increasing with age. The rate of H_2 increase was similar for both 0° and 20°C stored cells, see Figure 1. The maximum H_2 observed in these cells (50 months at 40°C) could be attributed to a reaction of lithium with ~50 ppm H_2O in the electrolyte.

Elements detected on the lithium anode by Auger Electron Spectroscopy (AES) and Electron Spectroscopy for Chenical Analysis (ESCA) include bromine, carbon, chlorine, oxygen and sulfur. Species seen on the anode by Fourier Transform Infra Red (FTIR) analysis include hydroxide and dithionite. Various sulfur species on the surface, as determined by X-ray Photoelectron Spectroscopy (XPS) included sulfur, sulfide, sulfite, sulfate and dithionite.

In general, dithionite is present in all the cells at approximately the same level; sulfate is present primarily in the newer cells; sulfite is present in higher concentrations in cells that have been stored at low temperature; and sulfide concentration is greater in cells that have seen higher storage temperatures.

A sample of each anode was bent sharply to crack the film. SEM and electron microprobe were used to characterize the film's cross section and AES was used to characterize the composition of the film inside the crack. In general, the film was thicker for the older cells. The newer cells exhibited a crystalline deposit on the surface, which became more amorphous with cell age.

No noticeable difference was observed in the electrolyte or cathodes of the various cells.

<u>Discharge tests</u>. As expected, capacity decreased with age at constant storage temperature and decreased with increasing storage temperature.

An Arrhenius plot was constructed utilizing the data from the various storage conditions, the high temperature aging tests on lots 5, 6 and 7 (0°C storage) and prior Sandia studies. The data have been normalized to Ah capacity lost per year, Figure 2. An activation energy of 10.26 Kcal/mole has been calculated for the cell degradation process. The dashed line in Figure 2 represents the upper 95% confidence limit for the data, i.e., one has 95% confidence that the average capacity loss will be below this line.

The rate of capacity loss has been calculated for several temperatures and is given in Table 1. The average value and the upper 95% confidence limit are listed for each temperature. In estimating capacity loss on storage, the confidence limit should be used. As can be seen, the Li/SO_2 system has an excellent shelf life if it is maintained at or below room temperature. For example, cells stored for 10 years at 0°C will lose <0.5 Ah. However, other factors need to be considered when using cells that have been stored for extended periods, e.g., voltage delay.

Conclusions

Storage and discharge tests were conducted on Li/SO_2 cells. The cells, comprising numerous lots from several manufacturers, were stored for up to seven years at temperatures ranging from -40°C to +60°C. An Arrhenius plot was constructed from the data and an activation energy of 10.26 Kcal/mole was calculated.

Chemical analysis of the cells indicated that H_2 gas is generated during storage, resulting in a slight increase in internal pressure. The maximum amount of H_2 observed can be accounted for by the presence of ~50 ppm H_2O in the electrolyte. The presence of H_2 does not appear to affect the performance or safety of the Li/SO_2 cells.

The Li/SO_2 cell has an excellent shelf-life when maintained at or below room temperature.

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Table 1. Capacity loss (Ah/yr) for Li/SO_2 D cells.

STORAGE TEMP. °C	AVERAGE	UPPER 95% CONF
-40	0.001	0.002
-20	0.005	0.009
0	0.026	0.038
20	0.095	0.119
40	0.294	0.368
60	0.782	0.918

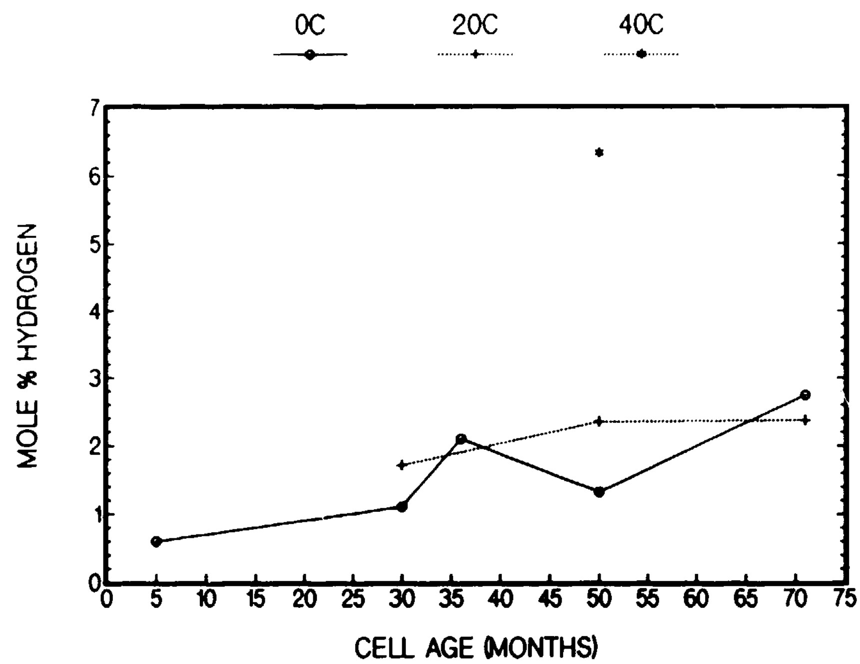

Figure 1. Hydrogen content vs. age of Li/SO_2 cells.

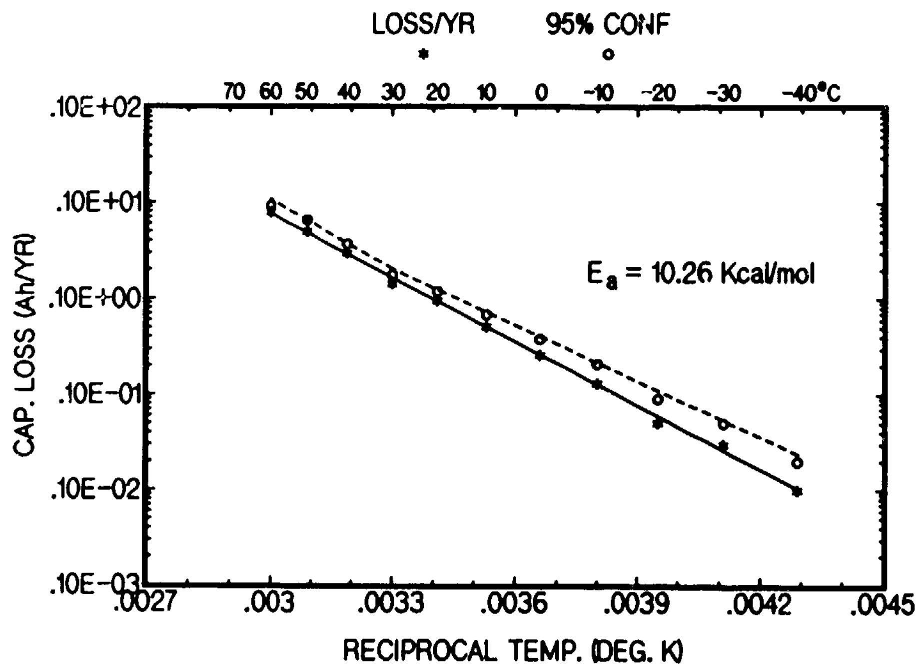

Figure 2. Arrhenius plot for Li/SO_2 cells.